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Report No. 8926-167

Material - Finishes and Coatings - Primer Pigments
Salt Spray Corrosion Resistance

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Abstract:

Five pigments, potassium zinc chromate; calcium chromate; strontium chromate; barium chromate; and zinc tetroxychromate, were incorporated with two different paint vehicles, an alkyd resin and a coumarone - indene resin vehicle, suitable driers and solvents, and applied to clad 7075-T6 aluminum alloy, AZ31, Condition H magnesium alloy, normalized 4130 steel, and annealed Type 321 stainless steel. The several samples were exposed to 20 percent salt spray exposure for 1500 hours to observe weight losses resulting from the corrosion exposure. The weight loss data showed the effectiveness of the five pigments when applied to steel and magnesium alloy ranked in the order they are mentioned above. Those primers formulated with alkyd resin vehicle performed better when applied to alloy steel and magnesium alloy than those formulated with the cumarone - indene resin.

Reference: Mappus, L. A., Whidden, R. H., Sutherland, W. M., "Chromate Pigments - Relative Efficiency in Aircraft Primers of," General Dynamics/Convair Report MP 56-264, San Diego, California, 27 December 1956. (Reference attached).

ENGINEERING TEST LABORATORIES

CONVAIR

A DIVISION OF GENERAL DYNAMICS CORPORATION

SAN DIEGO

REPORT 56-264

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TITLE

REPORT NO. 56-264
CHROMATE PIGMENTS -
RELATIVE EFFICIENCY IN
AIRCRAFT PRIMERS OF

MODEL MRS 56-185

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REPORT NO. 56-264
CHROMATE PIGMENTS -
RELATIVE EFFICIENCY IN AIRCRAFT PRIMERS OF

INTRODUCTION:

Potassium zinc chromate has been used exclusively as a corrosion inhibitive pigment in the aircraft industry. A literature search revealed that other chromate pigments might be more satisfactory, especially under conditions of high heat or in acid environments. These conditions are being encountered on today's fighter type aircraft due to high speeds and missile exhaust gases. The most recent comprehensive comparison of the efficiencies of various chromate pigments is that of H. G. Cole (Reference 1.).

This work was intended to be a partial replicate of the work done by Mr. Cole. Originally, it was planned to include an alkaline pigment, especially for magnesium and steel protection, and barium potassium chromate (Pigment E). However, a supplier could not be located for these two pigments. The following five chromate pigments were selected for evaluation: potassium zinc chromate; strontium chromate; calcium chromate; barium chromate; and zinc tetroxy-chromate. These pigments were formulated into priming paints using a coumarone-indene vehicle and also an alkyd vehicle similar to that used in specification MIL-P-8585 primer. The primers were applied to a clad aluminum alloy, a magnesium alloy, a chromium-molybdenum alloy steel, and a stainless steel. Test conditions for evaluation were the standard 20% salt spray cabinet and an exterior exposure with two daily sprays of sea water.

This report covers the results obtained after 1500 hours salt spray exposure on the magnesium and chromium-molybdenum alloy steel specimens. Addendum reports will be issued on the other specimens as soon as the results become significant.

OBJECT:

To determine the relative efficiency of five different chromate pigments as corrosion inhibitors in primer formulations, using a coumarone-indene resin vehicle and also the MIL-P-8585 alkyd vehicle, on four typical aircraft construction metals.

CONCLUSIONS:

1. The relative overall performance of the five pigments tested after 1500 hours salt spray exposure on magnesium and 4130 steel specimens was as follows, in the order of decreasing effectiveness:

   (a) Potassium zinc chromate
   (b) Calcium chromate
   (c) Strontium chromate
   (d) Barium chromate
   (e) Zinc tetroxychromate

CONCLUSIONS, (Cont'd.)

2. As a group, the primers formulated with the alkyd resin vehicle performed better than those formulated with the coumarone-indene resin vehicle on magnesium and steel specimens after 1500 hours salt spray exposure.

MATERIALS:

Metals -

Clad 7075T6 aluminum alloy, QQ-A-287
Magnesium alloy, QQ-M-44, AZ 31, Cond. H
4130 steel, AN-QQ-S-685, normalized
18-8 stainless steel, MIL-S-6721, Type 321, annealed

Pigments -

Potassium zinc chromate, Reichhold Chemicals # 1425
Strontium chromate, Mineral Pigments Corp. # 1365
Calcium chromate, Mineral Pigments Corp. # 1376
Barium chromate, Mineral Pigments Corp. # 1355
Zinc tetroxychromate, Reichhold Chemicals # 1430

Vehicles -

Coumarone-Indene, Neville Chem. Co. # R-12-A
Linseed oil, 900 poise, Archer-Daniels-Midland
Maleic anhydride, Barrett Chemical Co.
Phenol aldehyde, Bakelite # BKS 3962
Alkyd resin, Reichhold Chemicals # P-372

Driers -

Manganese drier, 6% solids, Nuodex
Cobalt drier, 6% solids, Nuodex
Lead drier, 24% solids, Nuodex

Solvents -

Naphtha (12-15% aliphatic), Neville Chem. Co. # 250W
Xylol, McGuire Chemical Co.
Butyl Alcohol, Union Carbide Corp.

TEST SPECIMEN PREPARATION:

Metal substrates- The composition of the alloys selected for test is shown in Table I. Specimens for each alloy were cut from a single sheet of material to assure uniformity of composition. Representative samples of each sheet were analyzed by the Chemical Laboratory. All specimens were .064 x 3 x 4 inches. The edges and corners of the specimens were rounded by filing.

TEST SPECIMEN PREPARATION, (Cont'd.)

Metal substrates, (Cont'd.) -

The aluminum alloy specimens were solvent wiped with methyl ethyl ketone, vapor degreased with trichoroethylene, alkaline cleaned and chromic acid anodized per MIL-A-8625, Type I.

Magnesium alloy specimens were vapor degreased, alkaline cleaned and dichromate treated in accordance with MIL-M-3171, Type III.

The 4130 steel specimens were sandblasted and solvent wiped prior to painting.

Stainless steel specimens were vapor degreased and passivated with nitric acid.

Paint formulation - All of the experimental primers were formulated for this test by the U. S. Paint and Chemical Co., 1133 Mariposa Street, San Francisco, California. Details of the formulations are shown in Tables III and IV. Unlike the Cole report, no final adjustment was made for gloss after manufacture. Details on the pigments used for formulations are shown in Table II.

Paint application - All of the primers were thinned with toluene to a Zahn # 1 viscosity of 40 at 77°F. prior to application. Specimens receiving the same primers were sprayed in the same batch to assure a uniform coat on the various substrates. Primers were applied within 24 hours after the metals were surface treated. After priming with one good cover coat, the specimens were allowed to cure at least 24 hours and then all specimens were top coated with MIL-L-7178 lacquer, color no. 514 black. The specimens were allowed to cure for two weeks prior to exposure.

Controls - Unpainted surface treated specimens of each alloy were used as controls.

TEST PROCEDURE:

Salt spray cabinet exposure - Specimens were exposed in quadruplicate to 20% salt spray in accordance with QQ-M-151A. All specimens were mounted at an angle of 20 degrees from the vertical in a single rack (see Figure 1.). Each of the quadruplicate specimens was exposed at a different level on the rack. Specimens of each of the four alloys were sub-grouped together. Control specimens were placed between those painted with coumarone-indene vehicle primers and those painted with the alkyd vehicle primers.

Exterior exposure - Quadruplicate specimens mounted at an angle of 45 degrees were exposed on a rack facing south (see Figure 2.). The rack was located approximately 1/2 mile inland from San Diego Bay. The specimens were attached to the rack with wooden pegs. Twice every working day, the specimens were sprayed with sea water which had been collected in the neighborhood of the whistle buoy at the entrance to San Diego harbor.

TEST PROCEDURE, (Cont'd.)

Evaluation procedure - Corrosion was evaluated by weight loss, expressed as grams per square decimeter per ounce of paint applied per square yard of surface. All specimens were weighed to the nearest tenth of a milligram at the following intervals:

(1) After surface treatment
(2) After priming
(3) After top coating
(4) After exposure (paint and corrosion products removed)

A paint stripper conforming to MIL-R-8633 was used to remove paint from the specimens.

Corrosion products were removed from the magnesium alloy specimens by immersing overnight in a cold 10% solution of ammonium chromate through which a stream of air was bubbled.

Lorayne Rust Remover, a proprietary material manufactured by Kruse Products Co. of LaMesa, California, was used to de-rust the 4130 steel specimens. This product was selected because of its negligible etching effect on 4130 steel (Reference TN 8811).

In addition to the weight loss evaluation, the magnesium and 4130 steel specimens were visually examined and rated after 1500 hours salt spray exposure prior to the removal of paint and corrosion products.

RESULTS:

These results are based on 1500 hours exposure to salt spray on magnesium and 4130 steel specimens only. Results are tabulated in Tables V, VI, VII, and VIII.

Performance of the potassium zinc chromate pigment was relatively good in both vehicles on magnesium and 4130 steel specimens.

There is no significant difference between the performance of the strontium chromate and the potassium zinc chromate in the alkyd vehicle on either magnesium or 4130 steel specimens.

The overall performance of calcium chromate was almost as good as the potassium zinc chromate.

Efficiency of the barium chromate was poor compared to the above three pigments but much better than the zinc tetroxychromate except in the alkyd vehicle on 4130 steel specimens.

Performance of zinc tetroxychromate was significantly poor in both vehicles on magnesium alloy specimens.

DISCUSSION OF RESULTS:

In drawing conclusions from this data, it must be remembered that only two alloys under an artificial exposure condition, namely magnesium and 4130 steel alloys after 1500 hours salt spray exposure, are being considered. Results will be more significant after the completion of the exterior exposure test.

Performances of the strontium chromate and calcium chromate were not exceptional enough on the tests completed to date to warrant substitution for potassium zinc chromate in all primer formulations. Perhaps these pigments may be used advantageously under conditions of high temperature, acidic environment, or in cases where potassium zinc chromate is incompatable with the vehicle, such as in amine catalyzed epoxy primers.

Corrosion on the magnesium specimens coated with zinc tetroxychromate pigmented primers was of the concentrated cell type, indicating that the relative insoluble nature of this pigment may have something to do with its poor performance. Zinc tetroxychromate is currently used in Military Specification wash primers. The Paint Research Department of the Sherwin-Williams Company has found that substitution of strontium chromate and silicon dioxide as the pigmentation in MIL-C-15328A wash primer improved its performance on magnesium (Reference 2.).

RECOMMENDATIONS:

It is recommended that this study be continued until the exterior exposure test results become significant.

REFERENCES:

1. "Tests on the Relative Efficiency of Chromate Pigments in Anticorrosive Primers", by H. G. Cole, J. Appl. Chem., 5 May 1955.

2. "Protective Coatings for Magnesium", The Sherwin=Williams Company, WADC Technical Report 54-373.

NOTE: The data from which this report was prepared may be found in Engineering Test Laboratories Data Book # 979.

TABLE I

COMPOSITION OF METAL SUBSTRATES

Composition by Analysis, %

Metal	Al	Zn	Mn	Fe	Cu	Ni	Si	P	S	Ti	Mo	Cr	C	Mg
Aluminum Alloy (Clad only)	Remainder	2.17			.35		.04							.49
Mag. Alloy	2.85	.89	.32	<.002	<.03	<.002	<.02							Remainder
4130 Steel			.56	Remainder			.35	.013	.015		.20	.91	.32	
18-8 Steel			1.48	Remainder		9.94	.84	.022	.005	.43		17.68	.07	

TABLE II

DETAILS OF PIGMENTS TESTED

Pigment	Manufacturer	Mfg. No.	Composition, % by weight						
			CrO_3	Alkali or Alkaline Earth		Zinc or Cadmium		Cl	SO_4
Potassium zinc chromate	Reichhold Chem., Inc.	#1425	43.8	10.0	K_2O	38.8	ZnO	nil	nil
Strontium chromate	Mineral Pigments Corp.	#1365	47.1	48.8	SrO			Trace	Trace
Calcium chromate	Mineral Pigments Corp.	#1376	57.7	32.3	CaO				
Barium chromate	Mineral Pigments Corp.	#1355	39.1	59.9	BaO			.05	
Zinc tetroxychromate	Reichhold Chem., Inc.	#1430	17.4			69.7	ZnO	Nil	Nil

TABLE III

COUMARONE - INDENE RESIN VEHICLE PAINT FORMULATIONS

Formula No.	Pigment	Composition of paint, % by weight Pigment	Vehicle	Xylol	MnDrier	CoDrier	Butyl Alcohol	Wt/Gal. Lbs.	Pigment to binder ratio.(Wt.)
1.	Potassium zinc chromate	43.1	37.4	12.8	2.2	3.3	1.2	11.3	2.2
2.	Strontium chromate	48.5	40.8	5.7	1.8	3.3		11.8	2.5
3.	Calcium chromate	61.1	26.0	10.0	1.3	1.8		13.2	5.0
4.	Barium chromate	67.3	21.4	8.3	1.0	1.8		16.3	6.7
5.	Zinc tetroxychromate	39.2	31.4	24.8	1.8	2.8		10.7	2.4

Note: Composition of vehicle, % by Wt.: Coumarone - Indene resin 24.5 %; 900 - poise linseed oil 24.8 %; solvent naphtha (12 - 15% aliphatic) 50.6%.

Driers: Manganese drier, 6% solids; Cobalt drier, 6% solids.

TABLE IV

MIL-P-8585 ALKYD RESIN VEHICLE PAINT FORMULATIONS

Formula No.	Pigment	Composition of paint, % by Wt. Pigment	vehicle	Xylol	Pb Drier	Co Drier	Wt./Gal. Lbs.	Pigment to binder ratio. (Wt.)
6.	Potassium zinc chromate	42.8	33.9	22.6	.33	.08	11.5	2.2
7.	Strontium chromate	48.1	33.5	18.0	.33	.08	12.4	2.5
8.	Calcium chromate	64.1	22.6	13.2	.13	.05	14.8	5.0
9.	Barium chromate	72.7	19.1	8.0	.10	.04	17.1	6.7
10.	Zinc tetroxychromate	44.4	32.5	22.8	.19	.08	11.1	2.4

Note: Composition of vehicle, % by Wt.; Maleic anhydride, .7%; phenol aldehyde resin, 11%; alkyd resin, 46.3%; solvent, 42%.

Driers; Lead drier, 24% solids; cobalt drier, 6% solids.

TABLE V

RESULTS AFTER 1500 HOURS SALT SPRAY EXPOSURE, MAGNESIUM ALLOY SPECIMENS
COUMARONE - INDENE VEHICLE

Formula No.	Pigment	Ave. Wt. of paint Oz/Yd.^{2}	Wt. losses due to corrosion, gm/dm^2				gm/dm^2 Wt. loss per (oz/yd^2) paint	Relative rating	Relative rating (Visual)
1.	Potassium zinc chromate	2.24	.0054	.0072	.0059	.0055	.0027	1	1
				Ave. = .0060					
2.	Strontium chromate	2.61	.0206	.0246	.0405	.0226	.0103	3	3
				Ave. = .0271					
3.	Calcium chromate	3.36	.0081	.0172	.0099	.0122	.0035	2	2
				Ave. = .0119					
4.	Barium chromate	4.81	.204	.133	.163		.0346	4	4
				Ave. = .167					
5.	Zinc tetroxychromate	3.50	2.60	4.90	1.90		.8950	5	5
				Ave. = 3.13					
	Control - not painted	---	1.30	1.39	.97				
				Ave. = 1.22					

TABLE VI

RESULTS AFTER 1500 HOURS SALT SPRAY EXPOSURE, MAGNESIUM ALLOY SPECIMENS

MIL-P-8585 ALKYD VEHICLE

Formula No.	Pigment	Ave. Wt. of paint oz/yd^2	Weight losses due to corrosion, gm/dm^2				gm/dm^2 Wt. loss per oz/yd^2 paint	Relative rating	Relative rating (visual)
6.	Potassium zinc chromate	3.30	.0130	.0010	.0043	.0037	.0017	1	1=
				Ave. =	.0055				
7.	Strontium chromate	3.72	.0427	.0013	.0026	.0002	.0031	2	1=
				Ave. =	.0117				
8.	Calcium chromate	4.47	.0108	.0055	.0394	.0063	.0035	3	2
				Ave. =	.0155				
9.	Barium chromate	6.74	.239	.105	.419		.0229	4	3
				Ave. =	.1543				
10.	Zinc tetroxychromate	4.72	.825	2.48	.410		.2621	5	4
				Ave. =	1.238				
	Control-not painted		1.30	1.39	.97				
				Ave. =	1.22				

TABLE VII

RESULTS AFTER 1500 HOURS SALT SPRAY EXPOSURE, 4130 STEEL SPECIMENS
COUMARONE - INDENE VEHICLE

Formula No.	Pigment	Ave. Wt. of paint oz/yd^2	Weight losses due to corrosion, gm/dm^2				gm/dm^2 Wt. loss per oz/yd^2 paint	Relative rating	Relative rating (visual)
1.	Potassium zinc chromate	2.17	.137	.109	.131	.097	.0549	2	2
				Ave. = .119					
2.	Strontium chromate	2.50	.323	.300	.206	.209	.1041	4	3
				Ave. = .260					
3.	Calciim chromate	3.69	.114	.195	.234	.148	.0468	1	1
				Ave. = .173					
4.	Barium chromate	4.96	.585	.318	.382	.330	.0815	3	4
				Ave. = .404					
5.	Zinc tetroxychromate	3.67	.451	.541	.512	.561	.1405	5	5
				Ave. = .516					
	Control - not painted		6.12	6.01	5.47				
				Ave. = 5.87					

TABLE VIII

RESULTS AFTER 1500 HOURS SALT SPRAY EXPOSURE, 4130 STEEL SPECIMENS

MIL-P-8585 ALKYD VEHICLE

Formula No.	Pigment	Ave. Wt. of paint Oz/yd²	Weight losses due to corrosion, gm/dm²				gm/dm² Wt. loss per oz/yd² paint	Relative rating	Relative rating (visual)
6.	Potassium zinc chromate	5.76	.044	.171	.100	.105	.0280	2	1
				Ave. = .105					
7.	Strontium chromate	3.83	.105	.141	.064	.098	.0266	1	3
				Ave. = .102					
8.	Calcium chromate	4.35	.181	.119	.170	.293	.0411	4	4
				Ave. = .191					
9.	Barium chromate	6.74	.505	.627	.633	.657	.0898	5	5
				Ave. = .605					
10.	Zinc tetroxychromate	4.30	.112	.188	.115	.094	.0291	3	2
				Ave. = .125					
	Control - no paint		6.12	3.01	5.47				
				Ave. = 5.87					

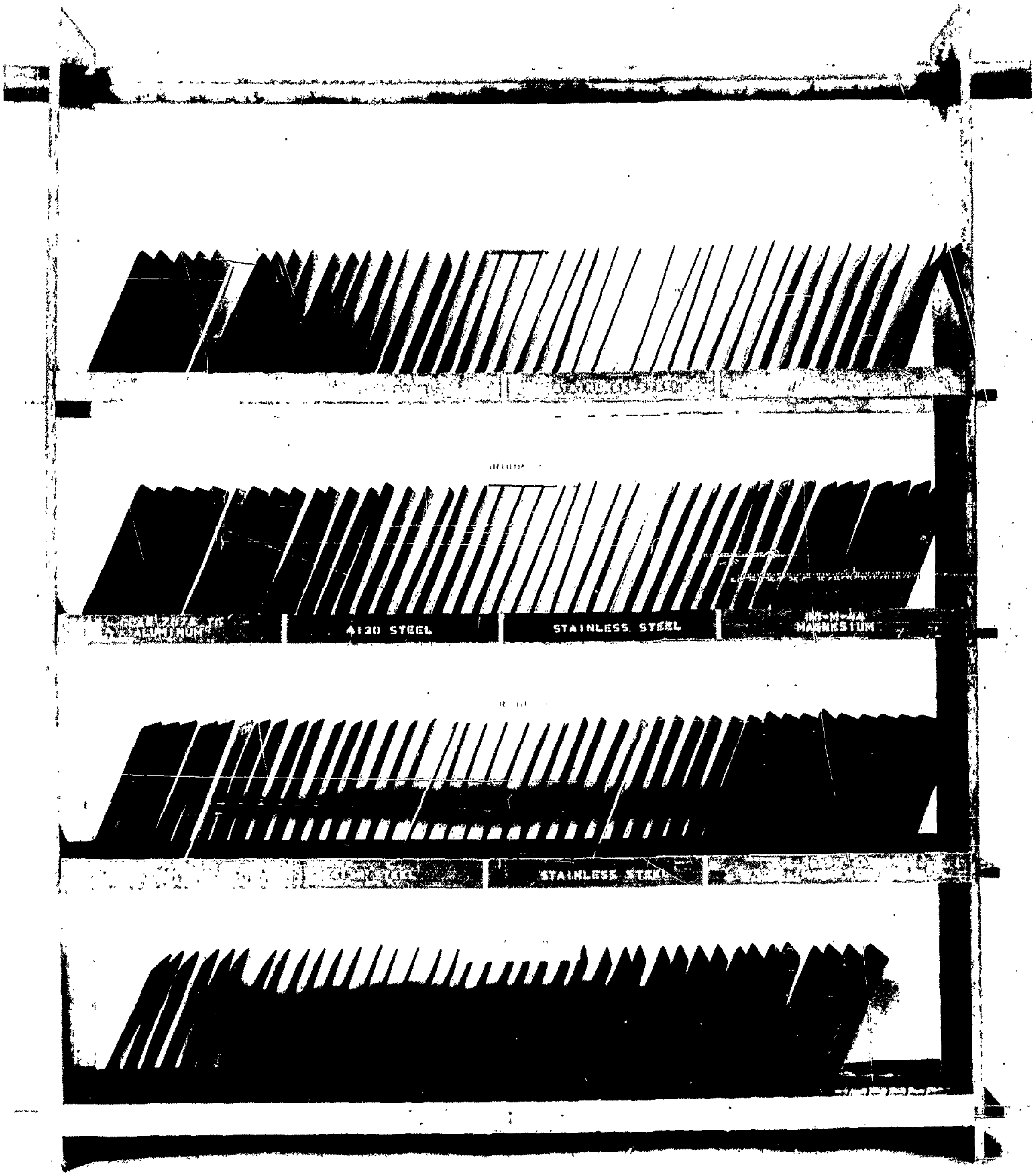

FIGURE 1

SPECIMENS PLACED IN SALT SPRAY EXPOSURE RACK

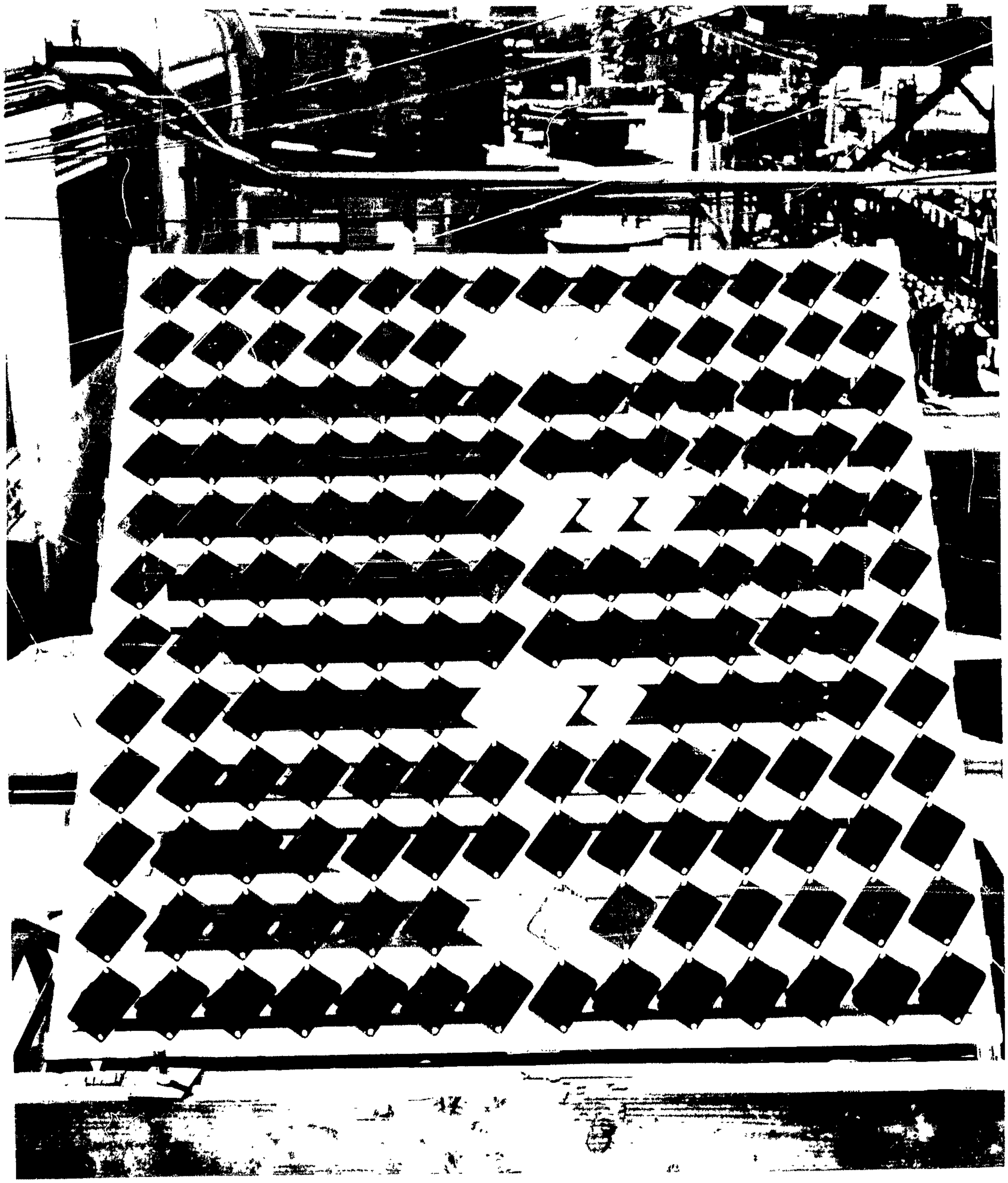

FIGURE 2

SPECIMENS MOUNTED ON EXTERIOR EXPOSURE RACK